The Use of Acrylic Compounds in Organic Synthesis. Part-1 (Commemoration Issue Dedicated to Professor Yuzo Inouye on the Occasion of his Retirement)

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Bull. Inst. Chem. Res., Kyoto Univ., Vol. 61, No. 2, 1983

REVIEW

The Use of Acrylic Compounds in Organic Synthesis. Part-1

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Received March 18, 1983

The previously reported reactions using acrylic compounds such as acrylonitrile, methyl and ethyl acrylate, and acrylamide are reviewed. The present article involves the reaction with the compounds having labile hydrogen atoms, the reaction with enamines, the Oxo reaction, the formation of phosphorus ylides, the reaction with sulfur ylides, the Ritter reaction as well as the transesterification.

KEY WORDS: Reaction of acrylonitrile/ Reaction of methyl acrylate/ Reaction of ethyl acrylate/ Reaction of acrylamide/

I. INTRODUCTION

One of the major objectives of modern organic synthesis is the finding of techniques for synthesizing useful and exciting compounds from easily available and relatively cheap starting materials. Some acrylic compounds such as acrylonitrile, methyl and ethyl acrylate, and acrylamide, which appear to be the parent compounds of a variety of acrylic compounds previously reported, may be included among these starting materials in organic synthesis. Owing to the widespread use of these acrylic monomers for the manufacture of synthetic rubber, adhesives, textile and paper coatings, leather finish resins, water emulsion paint vehicles, etc., many efforts have been devoted to the industrial preparation of these unsaturated compounds. The industrial preparation of acrylonitrile by the ammoxidation of propylene in the presence of suitable catalysts is well known as SOHIO process. There are two industrially important methods by which methyl and ethyl acrylate can be prepared, though many other processes have been reported. The first method is based on the reaction of acetylene and nickel carbonyl to give the hypothetical cyclopropenone, which, in the presence of methyl and ethyl alcohol, gives methyl and ethyl acrylate, respectively. Another, and generally preferred, production method for these acrylates starts from propylene, which is converted to acrolein and further to acrylic acid by air oxidation using suitable catalysts. The latter acid can then be converted to the acrylic esters by esterification. Thus, these acrylic monomers are readily made from very cheap raw materials, *viz.*, propylene, acetylene, ammonia, carbon monoxide, and methyl and ethyl alcohol. The emphasis of the reaction using them has been mostly on the preparation and development of useful high-polymers. On the contrary, little is recognized regarding

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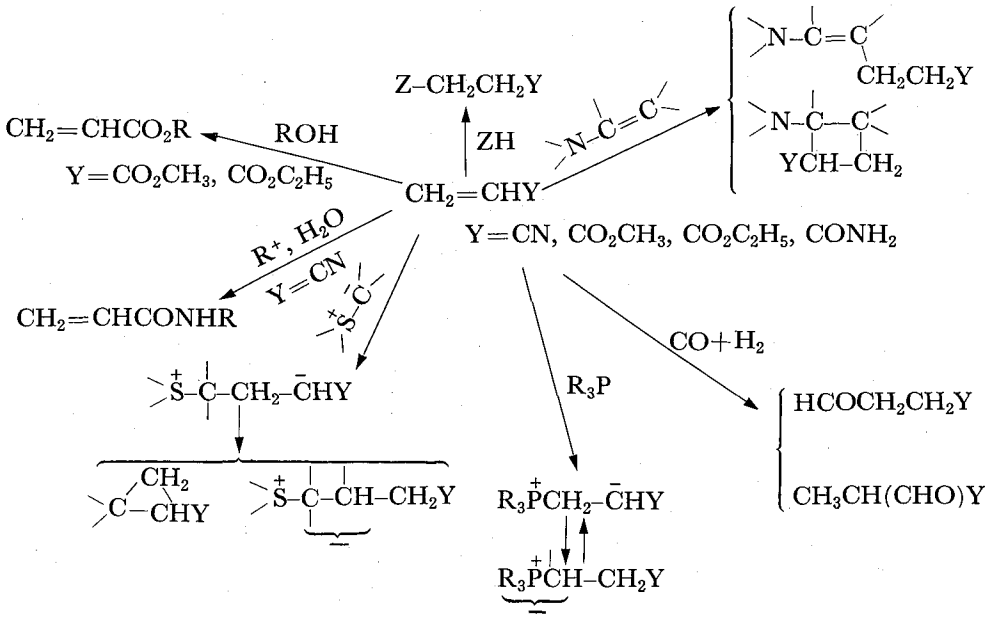
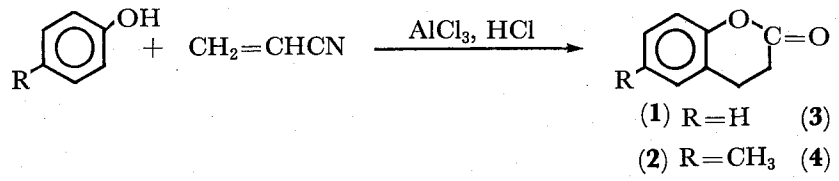
the role of these acrylic compounds in organic synthesis and related industry. The synthetic method for the preparation of monosodium *L*-glutamate involves the conversion of acrylonitrile to β-formlypropionitrile in a variation of the Oxo synthesis and the Strecker reaction with the resulting nitrile to provide α-aminoglutaronitrile followed by hydrolysis. However, the half part of the monosodium slat is even now manufactured by hydrolysis of protein or by fermentation. Accordingly, the finding of a novel reaction using these acrylic compounds as well as the making use of them in a variation of the known reaction may be a significant objective of organic synthesis. A better understanding of the previously reported reactions with these acrylic compounds will serve to attain the objective. Thus, in this and the continued reviews a survey is given of experimental results and some pertaining rationalization in the area of organic reactions in which acrylonitrile, methyl and ethyl acrylate or acrylamide participate. The classification used is based on the type of reaction and on the kind of reaction partner. The present paper deals with reactions of the acrylic compounds which seem to belong to the following sections; the reaction with the compounds possessing labile hydrogen atoms, the reaction with enamines, the hydroformlyation with carbon monoxide and hydrogen, the reaction of phosphorus ylides derived from acrylic compounds and the reaction with sulfur ylides as well as the Ritter reaction and the transesterification. These are schematically outlined below.



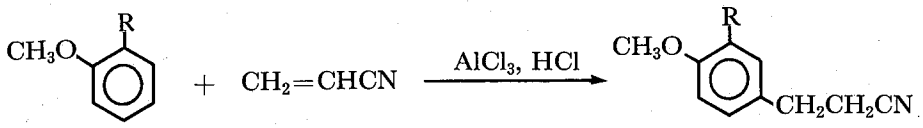
II. THE REACTION WITH THE COMPOUNDS POSSESSING LABILE HYDROGEN ATOMS

The utility of acrylonitrile, methyl and ethyl acrylate, and acrylamide as acceptors in the Michael reaction is well known. The literature is summarized in an earlier review[1] of this reaction. Under the influence of alkaline reagents, typically alkali metal alkoxides, the acrylic compounds react with a variety of compounds containing

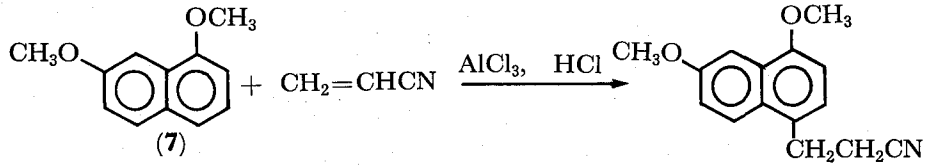
active hydrogen atoms such as malonates, cyano esters, keto esters, carboxylic acid esters, aldehydes, ketones, nitriles, nitro compounds, sulfones, to form the corresponding adducts. The Michael reaction using acrylonitrile as an acceptor results in the formation of molecules containing a β-cyanoethyl group at the location of the reactive hydrogen atom contained in a donor, and the reaction is commonly known as cyanoethylation. The scope, limitations, and experimental conditions as well as experimental procedures of cyanoethylation reactions have also been presented in an earlier review by Bruson.[2] Although it is impossible to introduce directly a cyanoethyl group into benzene itself, phenol, anisole and their certain derivatives undergo cyanoethylation by acrylonitrile on the benzene nucleus when the reaction is conducted in the presence of $AlCl_3$ plus HCl. Simple phenol, for example, forms β-(p-hydroxyphenyl)propionitrile in good yield.[3] Also, p-substituted phenols react with acrylonitrile to furnish dihydrocoumarin (**1**) and its derivatives **2**, **3**, and **4**.[4] This cyanoethylation is also possible with anisole (**5**)[5] and its derivatives such as **6**[5], **7**[5], and **8**.[6] The method has been further extended[7] to some derivatives of phenetole as well as methyl and ethyl ether of resorcinol as the starting materials. However, in the presence of alkaline catalysts such as alkali metals and alkoxides, phenol, resorcinol, and many of their derivatives are cyanoethylated on the hydroxyl groups to form the corresponding cyanoethyl ethers, indicating that the reactions occur in a manner similar to those of aliphatic alcohols with acrylonitrile.[2]



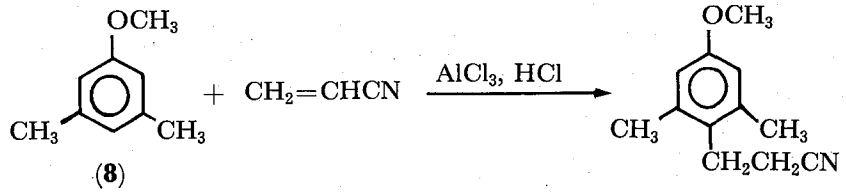
(**1**) R=H (**3**) R=OCH_3
(**2**) R=CH_3 (**4**) R=Cl



(**5**) R=H
(**6**) R=CH_3



(**7**)



(**8**)

Although the addition of the acidic compounds such as HCN, HCl, HBr, $NaHSO_3$ to acrylonitrile in the presence or absence of alkaline catalysts has been known for a long time it was only in 1968 that Javaid and his co-workers[8] found that free carboxylic acids also add to excess acrylonitrile at elevated temperature. In this and similar cases studied by Fujita and his co-woaker,[9] metallic Cu–$Cu(OH)_2$ has been found to act as a useful catalyst in the process. Best results are obtained[10] with $Cu[P(C_6H_5)_3]_2Cl_2$ as a catalyst than with the other Cu salts in the cyanoethylation of several carboxylic acids to afford the corresponding β-cyanoethyl carboxylates as shown.

$RCO_2CH_2CH_2CN$ $\quad$ $NCCH_2CH_2O_2C(CH_2)_nCO_2CH_2CH_2CN$

$R=CH_3$, C_2H_5, n-C_3H_7, n-C_7H_{15}, $CH_2=C(CH_3)$– $\quad$ $n=0$–4

The compounds having one or more –NH– groups such as primary and secondary amines, lactams, imides, and amides add to acrylonitrile with or without the aid of a catalyst. Many instances are listed in the reivew above mentioned.[2] Recently, the cyanoethylation reaction has been extended to many more complex primary and especially secondary amines. For example, the compounds **9** have been prepared[11] by reacting the corresponding alkylamines with acrylonitrile in the presence of acetic acid at 110–150°C. An aliphatic polyamine **10** is synthesized[12] by cyanoethylation of hexamethylenediamine followed by hydrogenation. Bis(3-dimethylaminopropyl)-amine and acrylonitrile, when refluxed in isopropyl alcohol, react to give a cyanoethylated triamine **11**.[13] The former **10** is useful as corrosion inhibitor, and the latter **11** is a good catalyst for manufacture of urethane polymer foams.

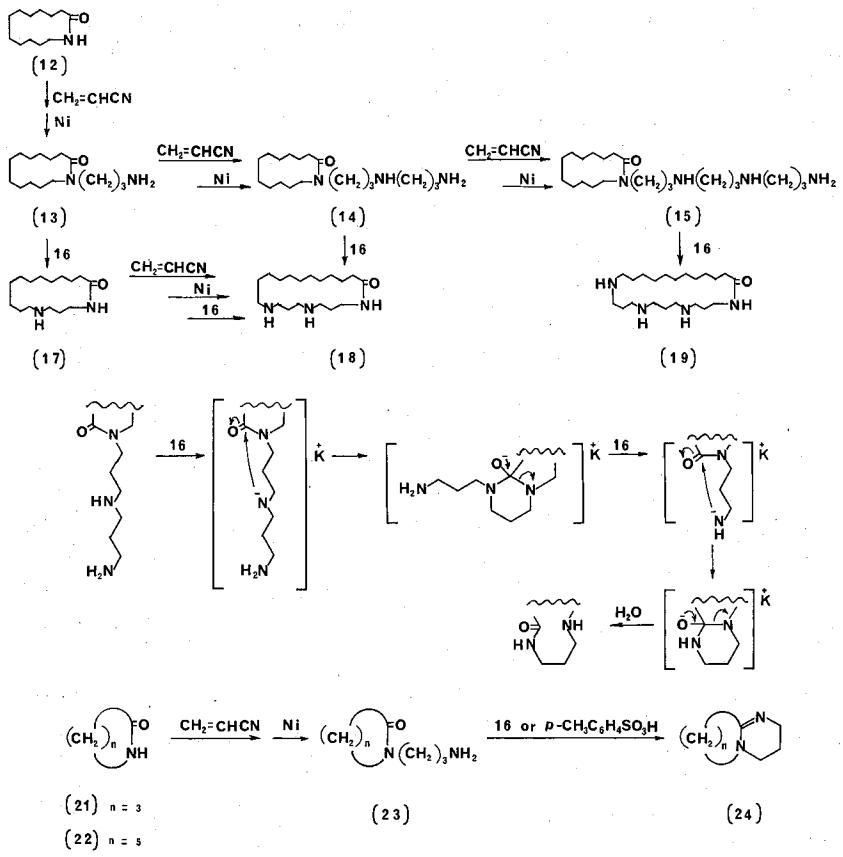
$CH_3(CH_2)_nN(CH_2CH_2CN)_2$ $\quad$ $(H_2NCH_2CH_2CH_2)_2N(CH_2)_6N(CH_2CH_2CH_2NH_2)_2$

(**9**) $n=3$–26 $\quad$ (**10**)

$[(CH_3)_2NCH_2CH_2CH_2]_2NCH_2CH_2CN$

(**11**)

A convenient procedure has been developed for the synthesis of some macrocyclic lactams by Kramer and his co-workers.[14] Cyanoethylation of **12** with acrylonitrile, followed by hydrogenation over Raney Ni, affords **13**, and repetition of this process once and twice gives **14** and **15**. When **13**, **14**, and **15** are treated with pottasium 3-aminopropylamide (**16**) in 1, 3-diaminopropane at room temperature, ring expansion take place to afford **17**, **18**, and **19**, respectively. The probable path is indicated in the accompanying equations. This procedure is also applicable[15] to 7-heptanel-actam (**20**) as a starting lactam. However, when 2-pyrrolidone (**21**) and ε-caprolactam (**22**) are submitted to this series of transformations, dehydration of the intermediate **23** to form **24** is observed.[15] The dehydration may be also brought about[16,17] by heating **23** with p-toluenesulfonic acid in xylene. Very often, the compounds **24** are used for removal of hydrogen halide from halides. Di-cyanoethylation takes place in the reaction between acrylamide and a large excess of acrylonitrile in the presence of sodium methoxide. When the resultant **25** is heated under reduced pressure, it undergoes decomposition to afford **26** and acrylonitrile.[18]



$$CH_2{=}CHCONH_2 + 2CH_2{=}CHCN \xrightarrow{CH_3ONa} CH_2{=}CHCON(CH_2CH_2CN)_2$$
(25)

$$\xrightarrow{\text{heat}} CH_2{=}CHCONHCH_2CH_2CN + CH_2{=}CHCN$$
(26)

Aldehydes and ketones in which the α-carbon atom has one or more hydrogen atoms add to acrylonitrile in the presence of alkaline catalysts. Thus, one, two, three, or more cyanoethyl groups are introduced into the methinyl, methylene, and methyl groups adjacent to the carbonyl group. The reaction has been considered in detail by Bruson[2] and later by Bergmann and his co-workers.[1] The behavior of acrylonitrile with some aromatic aldehydes in which an α-hydrogen is lacking in the presence of alkaline catalysts such as sodium methoxide, Triton B, and piperidine has also been reported.[19] However, the behavior of acrylonitrile with some aromatic and heterocyclic aldehydes in the presence of NaCN is rather interesting. For example, several γ-keto cyanides such as **27** are prepared[20] from the reaction of the corresponding aromatic and heterocyclic aldehydes with acrylonitrile using NaCN catalyst. In a similar manner, these aldehydes are reacted with ethyl acrylate in N, N-dimethylformamide to give the corresponding γ-keto esters **28**.[21] Stetter and his co-worker have examined the possibility of substituting another catalyst, 3-

benzyl-5-(2-hydroxyethyl)-4-methylthiazolium chloride (**29**), for NaCN employed in the above procedure and found[22] that both aromatic and heterocyclic as well as aliphatic aldehydes add similarly to acrylonitrile and to ethyl acrylate under the catalytic influence of **29** in the presence of triethylamine. When silver acetate is used to catalyze the reaction of butyraldehyde and methyl acrylate, methyl β-butyrylpropionate can be formed.[23] However, the mechanism of this reaction may be entirely different, involving attack by butyryl radical.

$$RCHO + CH_2{=}CHCN \xrightarrow{NaCN} RCOCH_2CH_2CN$$

(**27**)

R = C_6H_5, *p*–ClC_6H_4, *p*–BrC_6H_4, 2–$C_{10}H_7$, 3-pyridyl, 4-pyridyl, 2-furyl, 2-thienyl

$$RCHO + CH_2{=}CHCO_2C_2H_5 \xrightarrow{NaCN} RCOCH_2CH_2CO_2C_2H_5$$

(**28**)

R = C_6H_5, *p*–ClC_6H_4, 3–pyridyl, 2–thienyl

Like acrylonitrile, methyl and ethyl acrylate also react with free carboxylic acids at elevated temperature. For example, these acrylates containing small amounts of hydroquinone monomethyl ether react with acetic acid at 190°C in the presence of CuO to form β-(methoxy- and ethoxycarbonyl)ethyl acetate (**30**, R = CH_3 and **30**, R = C_2H_5). Further work involving conversion of propionic and butyric acid to the corresponding β-(methoxy- and ethoxycarbonyl) ethyl carboxylate is also patented.[24] Methyl acrylate reacts with ethyl fluorocarbamate in sulfuric acid to give methyl N-ethoxycarbonyl-N-fluoro-β-aminopropionate (**31**), the product of alkylation by the terminal position of the resonance-stabilized protonated ester.[25] The reaction of ethyl acetoacetate with ethyl acrylate in the presence of Triton B produce the adduct **32** after a NaOH-catalyzed hydrolysis. Grob and his co-worker[26] have found that heating **32** with potassium acetate leads to the cyclic compound **33**, which can be converted into **34** by the action of sodium ethylate.

$$CH_3CO_2H + CH_2{=}CHCO_2R \xrightarrow{CuO,\ 190°C} CH_3CO_2CH_2CH_2CO_2R$$

(**30**)

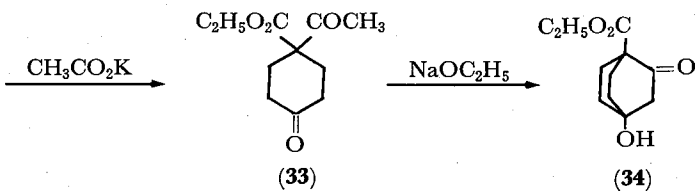
R = CH_3, C_2H_5

$$NHFCO_2C_2H_5 + CH_2{=}CHCO_2CH_3 \xrightarrow{H_2SO_4} CH_3O_2CCH_2CH_2NFCO_2C_2H_5$$

(**31**)

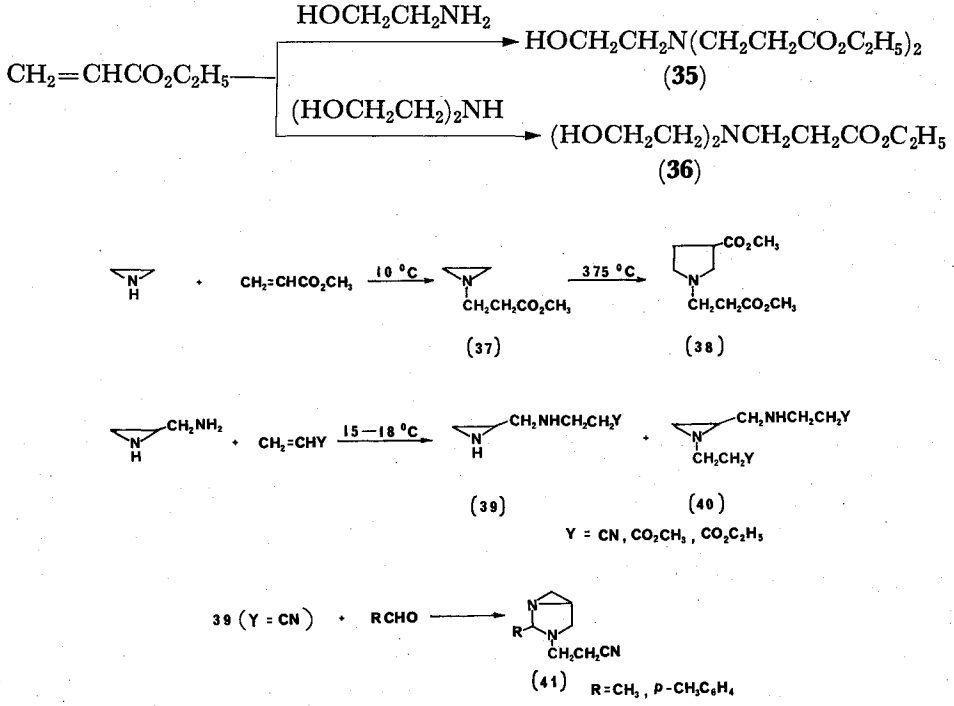
$$CH_3COCH_2CO_2C_2H_5 + CH_2{=}CHCO_2C_2H_5 \xrightarrow{\text{Triton B}} \xrightarrow{NaOH} \begin{matrix} CH_3CO \\ C_2H_5O_2C \end{matrix}\!\!>\!C(CH_2CH_2CO_2H)_2$$

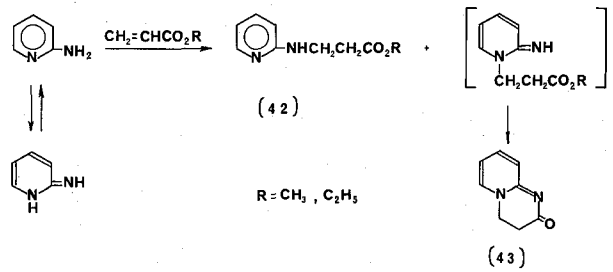
(**32**)



(**33**) (**34**)

At 40–50°C, ethyl acrylate reacts with ethanolamine and diethanolamine to give the adducts **35** and **36**, respectively. These adducts are treated with stearylamine at elevated temperature, reacted with ethylene oxide, and then quaternized with dimethyl sulfate for the production of revelling agents for dyeing.[27] The preparation of 3-dimethylamino-N, N-dimethylpropionamide is accomplished[28] by heating ethyl acrylate, dimethylamine, and small amounts of so-called inhibitors in an autoclave. This amide together with bis[2-(N, N-dimethylamino)ethyl]ether and triethylenediamine is used as a catalyst in the manufacture of flexible or highly resilient polyurethane foams. Ethyleneimine can react with one or two moles of methyl acrylate.[29,30] Low temperatures favor the addition of one molecule of ethyleneimine with formation of N, N-ethylene-β-alanine methyl ester (**37**); higher temperatures result in the addition of the initially formed **37** to a second molecule of methyl acrylate with formation of **38**. The reaction of 2-(aminomethyl)ethyleneimine with acrylic compounds such as acrylonitril, methyl and ethyl acrylate proceeds smoothly at room temperature to afford both the corresponding 1 : 1 adducts **39** and 1 : 2 adducts **40**. Among these adducts only one of **39**, in which Y=CN, is converted into diazabicyclohexanes **41** by treatment with aldehydes.[31] The reaction of 2-aminopyridine with alkyl acrylates gives not only a noncylic product, an alkyl ester of N-(2-pyridyl)-β-alanine (**42**) but also a cyclic product **43**.[32] The latter compound is formed by the attack of alkyl acrylates at the ring nitrogen of the imino form of 2-aminopyridine.





The carbamoylethylation of aliphatic alcohols having two or more hydroxyl groups is accomplished[33] by heating them with acrylamide in the presence of an alkaline catalyst. For example, diethylene glycol and acrylamide react in the presence of Triton B to yield **44**, which is further reacted with 1-butanol to afford the compound **45** that has found use as a plasticizer.[33] Some α-amino acids add in aqueous solution to acrylamide in the presence of KOH to give the 1: 1 adducts **46** or 1: 2 adducts **47**, depending upon the proportion of reagents.[34] Analogous behavior is also observed[35] in the reactiion of β-alanine with acrylamide in aqueous solution under the catalytic action of triethylamine. The carbamoylethylation reaction of primary and secondary amines is also known. The literature is summarized in an earlier review.[36]

$$(HOCH_2CH_2)_2O + CH_2{=}CHCONH_2 \xrightarrow{\text{Triton B}} (H_2NCOCH_2CH_2OCH_2CH_2)_2O \quad (\mathbf{44})$$

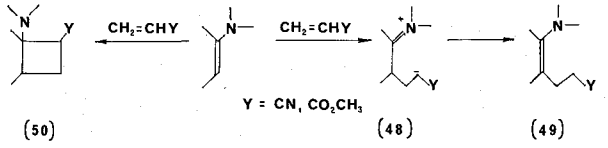
$$\xrightarrow{n\text{-}C_4H_9OH} (n\text{-}C_4H_9O_2CCH_2CH_2OCH_2CH_2)_2O \quad (\mathbf{45})$$

$$HO_2CCH(R)NH_2 + CH_2{=}CHCONH_2 \xrightarrow[H_2O]{KOH} HO_2CCH(R)NHCH_2CH_2CONH_2 \quad (\mathbf{46})$$

$$\xrightarrow[H_2O]{KOH} HO_2CCH(R)N(CH_2CH_2CONH_2)_2 \quad (\mathbf{47}) \qquad R=H,\ CH_3,\ C_2H_5,\ \textit{iso}\text{-}C_3H_7,\ \textit{iso}\text{-}C_4H_9,\ n\text{-}C_4H_9,\ p\text{-}HOC_6H_4CH_2$$

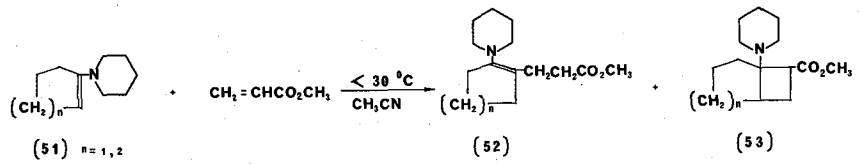
III. THE REACTION WITH ENAMINES

The addition of enamines to electrophilic olefins such as acrylonitrile or methyl acrylate has been shown to give the Stork alkylation products **49** and/or cycloaddition products **50** depending on choice of reactants and reaction conditions.

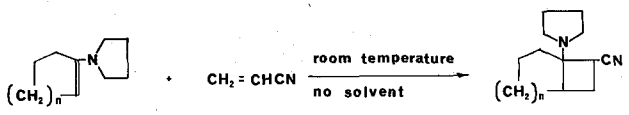


When the piperidine enamine of cyclopentanone (**51**, n=1) or of cyclohexanone (**51**, n=2) and methyl acrylate are allowed to react in acetonitrile without controlling the temperature, only the Stork alkylation product **52** is obtained.[37] When, however, the reaction mixture is maintained below 30°C, both **52** and the cycloaddition product **53** are produced.[37] Similar reactions have been found to occur when the dimethyl-

amine enamines of cyclopentanone and of cyclohexanone were used as the enamine component.[37] Fleming and his co-worker[38] have found that some enamines such as **54**, **55**, and **56** derived from pyrrolidine and alicyclic ketones react with acrylonitrile at room temperature to afford exclusively the corresponding cyclobutane derivatives (**57**, **58**, and **59**), respectively. Also, when the reaction of β-hydrogen-containing enamines derived from aldehydes or the only acyclic ketone studied, 3-pentanone, with acrylonitrile or with methyl acrylate is carried out under properly mild conditions, the occurrence of the Stock alkylation is prevented and only the cycloaddition product is produced.[39] For example, the piperidine enamine (**60**) of butyraldehyde give, with methyl acrylate, the cyclobutane derivative **61** when the reaction is carried out in acetonitrile for 2 days at room temperature.[39] Enamines containing no β-hydrogen are incapable of undergoing the Stork alkylation; they react with electrophilic olefins such as acrylonitrile or methyl acrylate to give only the cyclobutane derivatives on heating the reactants at elevated temperature in an autoclave or, better, by refluxing in acetonitrile.[39] However, it is very difficult to determine which course the reaction of these electrophilic olefins with enamines having β-hydrogens would take. Yamada and his co-workers[40,41] have found that *L*-proline alkyl ester enamines (**62**) of cyclohexanone react with methyl acrylate and with acrylonitrile to give, after hydrolysis, *S*-2-(2-methoxycarbonyl- and 2-cyanoethyl)cyclohexanones (**63**, $Y=CO_2CH_3$ and **63**, $Y=CN$), respectively. This is a rare case in which the reaction course may be easily determinable although the employed enamines possess β-hydrogens. Presumably, steric hindrance in **62** may operate which tend to depress the occurrence of cycloaddition reaction. The Stork alkylation above described involves nucleophilic attack by the enamine carbon on the electrophilic carbon of acrylonitrile or of methyl acrylate, with the generation of a zwitterionic intermediate **48**, and it was developed largely by Stork and his co-workers whose extensive paper[42] describes the technique and range of the reaction. On the other hand, the cycloaddition reaction, leading to a cyclobutane derivative, could proceed either from a zwitterionic intermediate similar to **48** by intramolecular attack, or by direct cycloaddition of the enamine to the acrylic compounds, and it offers a very simple and frequently high-yield route to the cyclobutane derivatives. No cycloaddition product is obtained from the reaction of 1-ethoxy-N, N-dimethylvinylamine with methyl acrylate. Instead, the Stork alkylation product **64** is obtained.[43] 1-Ethoxy-N, N, 2-trimethylpropenylamine react with methyl acrylate to give the cyclobutene derivative **65**, but in poor yield, presumably by loss of alcohol from the initially formed cyclobutane derivative.[43] In general, secondary enamines such as **66** are thermodynamically unstable since they exist in equilibrium with the tautomeric imines **67**. Recently, Jeso and his co-worker[44] have obtained pure secondary enamines by partial methanolysis of organo-tin or magnesium salts of imines. The secondary enamines thus obtained are quite stable at $-80°C$, and undergo the attack of acrylonitrile at $0°C$, leading, besides some polymerization, to the adducts **68**.

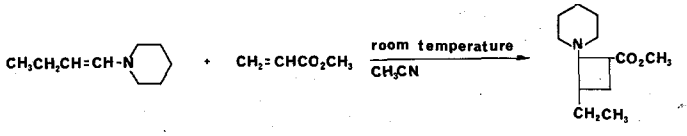


(51) n = 1, 2 (52) (53)

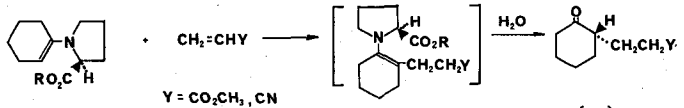


(54) n = 1
(55) n = 2
(56) n = 3

(57) n = 1
(58) n = 2
(59) n = 3



(60) (61)



(62) (63)

R = CH_3, C_2H_5, *tert*-C_4H_9

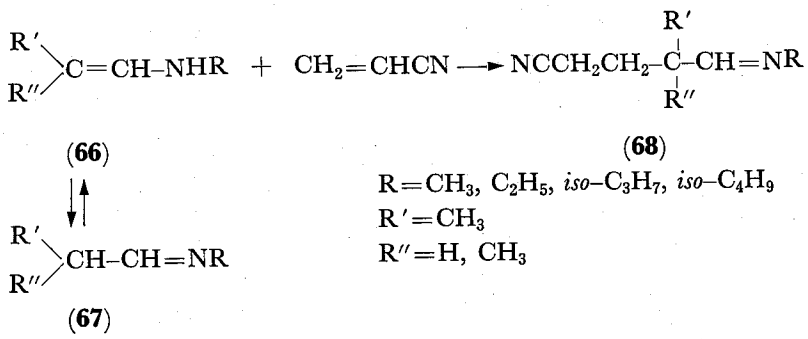
$$CH_2{=}C(OC_2H_5){-}N(CH_3)_2 \;+\; CH_2{=}CHCO_2CH_3 \xrightarrow[\text{no solvent}]{20\text{—}60^\circ C} CH_3O_2CCH_2CH_2CH{=}C(OC_2H_5){-}N(CH_3)_2$$

(**64**)

$$(CH_3)_2C{=}C(OC_2H_5){-}N(CH_3)_2 \;+\; CH_2{=}CHCO_2CH_3 \xrightarrow[CH_3CN]{\text{reflux}} \left[\begin{array}{l}(CH_3)_2\\(CH_3)_2N\end{array}\!\square\!\begin{array}{l}CO_2CH_3\\OC_2H_5\end{array}\right]$$

$$\xrightarrow{-C_2H_5OH} \begin{array}{l}(CH_3)_2\\(CH_3)_2N\end{array}\!\square\!\!=\!\!CO_2CH_3$$

(**65**)



IV. THE HYDROFORMYLATION WITH CARBON MONOXIDE AND HYDROGEN

$$CH_2{=}CHY + CO + H_2 \xrightarrow{\text{catalyst}} HCOCH_2CH_2Y + CH_3CH(CHO)Y$$
$$Y{=}CO_2CH_3,\ CO_2C_2H_5,\ CN$$

The Oxo reaction originally consisted of the treatment of an olefin with water gas or synthesis gas in the presence of a cobalt catalyst to produce aldehydes containing 1 carbon atom more than the starting olefin. The reaction was also carried out with some acrylic compounds instead of the olefins. The reaction results in the addition of the units of formaldehyde, H–CHO, across the double bond of the applied acrylic compounds. It is apparent that the addition can lead to one or the other of two compounds or to a mixture of both, depending on which carbon atom of the acrylic compound adds the formyl group. For example, the product from ethyl acrylate in the Oxo reaction is usually a mixture of ethyl α- and β-formylpropionate. The proportion of them is affected by various reaction conditions as is well illustrated by Takegami and his co-workers[45] who studied in detail the effects of reaction conditions on the distribution of the products in the $Co_2(CO)_8$-catalyzed hydroformylation of ethyl acrylate in toluene. Cobalt tricarbonyl modified by PR_3($R=C_6H_5$, cyclohexyl, n–C_4H_9), $[Co(CO)_3PR_3]_2$,[46] and Rh_2O_3[47] are also known to be active catalysts for the hydroformylation of methyl and ethyl acrylate. Tanaka and his co-workers[48] studied the $Rh_2Cl_2(CO)_4$-catalyzed hydroformylation of ethyl acrylate at 150°C under 100 atm of synthesis gas in the absence or presence of various additional phosphorus ligands, and found that in order to attain a high selectivity of α-formylation (>95%) leading to ethyl α-formylpropionate, the addition of shorter methylene-chained diphosphines [$R_2P(CH_2)_nPR_2$, $R=C_6H_5$ or cyclohexyl, n=2–4] to the reaction system was essential, while the use of $Rh_2Cl_2(CO)_4$ alone or in combination with triphenylphosphine or a diphosphine having a longer methylene chain, $(C_6H_5)_2$-$P(CH_2)_5P(C_6H_5)_2$, resulted in a very low yield of ethyl α-formylpropionate. Besides, it has been noted in a patent claim[49] that the highest α-selectivity (>99%) in the hydroformylation of methyl acrylate in cyclohexane could be accomplished by the use of $HRh(CO)(PR_3)_3$, in which $R=C_6H_5$, together with triphenylphosphine. If the Oxo reaction of methyl and ethyl acrylate in benzene was performed at 250°C and at about 300 atm by using a catalytic amount of $Co_2(CO)_8$, the main product was γ-

butyrolactone (**69**).[50,51] Presumably, the initially formed methyl and ethyl β-formylpropionate were reduced to the corresponding alcohols under the reaction conditions, which were further converted into **69**, suggesting that $Co_2(CO)_8$ also favors β-formylation under the above reaction conditions.

$$CH_2{=}CHCO_2R + CO + H_2 \xrightarrow{Co_2(CO)_8,\ 250°C,\ 300\ atm} \underset{R=CH_3,\ C_2H_5}{\text{(69)}}$$

The product from acrylonitrile in the $Co_2(CO)_8$-catalyzed Oxo reaction is usually a mixture of α- and β-formylpropionitrile, but the former is in relatively small amounts. As described in the preface of this review, β-formylpropionitrile has found a particularly important use in the preparation of monosodium *L*-glutamate. Thus, many efforts have been devoted to the industrial preparation of this nitrile. Many chemists of Aginomoto Co., Inc. in Japan have also carried out considerable experiments and presumably pooled their knowledge concerning the preparation of β-formylpropionitrile from acrylonitrile. We cannot reveal here the pooled knowledge, and hence only the published literature of the hydroformylation of acrylonitrile will be summarized below. If the $Co_2(CO)_8$-catalyzed reaction was run in a polar solvent such as methyl alcohol or acetone, a higher selectivity of β-formylation leading to β-formylpropionitrile could be accomplished than that obtained in the reaction with a nonpolar solvent such as benzene.[52] Further, Kashina and his co-workers[53] have found that the $Co_2(CO)_8$-catalyzed hydroformylation of acrylonitrile in methyl alcohol gave a 1 : 10 mixture of α- and β-formylpropionitrile together with a small amount of methyl α-cyanopropionate. The addition of a small amount of diethylamine, N, N-dimethylaniline or pyridine also facilitates the formation of β-formylpropionitrile in the $Co_2(CO)_8$-catalyzed hydroformylation of acrylonitrile in benzene.[54] Noyori and his co-workers[55,56] have proposed two unique methods by which the isolation of the desired β-formylpropionitrile is easily achieved. When a solution of acrylonitrile and a small amount of $Co_2(CO)_8$ in benzene was heated with a 1 : 2 mixture of carbon monoxide and hydrogen at 120°C and at pressures over 240 atm and further at 200°C, β-hydroxy-α-methylpropionitrile (**70**), γ-hydroxybutyronitrile (**71**), and ethyl cyanide were obtained in yields of 12, 56, and 16%, respectively.[57] The former two of them are the compounds which were formed by subsequent reduction of the initially produced α- and β-formylpropionitrile. Other catalysts such as Rh_2O_3,[58] $[Co(CO)_3P(n\text{-}C_4H_9)_3]_2$,[59] and $Co_2(CO)_8$ in combination with porphyrins[60] can also be used for the reaction of acrylonitrile with carbon monoxide and hydrogen. When acrylamide was submitted to the reaction with carbon monoxide at 200°C and at 300 atm under

$$CH_2{=}CHCN + CO + 2H_2 \xrightarrow{Co_2(CO)_8,\ 120°C \text{ and further } 200°C,\ 240\ atm}$$
$$[HCOCH_2CH_2CN] + [CH_3CH(CHO)CN] + C_2H_5CN$$
$$\downarrow \qquad\qquad \downarrow$$
$$HOCH_2CH_2CH_2CN \qquad CH_3CH(CH_2OH)CN$$
$$\text{(71)} \qquad\qquad \text{(70)}$$

$$CH_2{=}CHCONH_2 + CO \xrightarrow{Co_2(CO)_8,\ 200°C,\ 300\ atm} \text{(succinimide)}$$

the catalytic action of $Co_2(CO)_8$, it was easily converted to succinimide.[61]

V. THE REACTION OF PHOSPHORUS YLIDES DERIVED FROM ACRYLIC COMPOUNDS AND THE REACTION WITH SULFUR YLIDES

In the presence of several alcohols, triphenylphosphine catalyze the conversion of acrylonitrile to a high-melting, insoluble hexamer **74**.[62] As shown in the following equations, this reaction is believed to proceed by the initial formation of a betaine intermediate **72** which gives rise to the corresponding phsphorus ylide **73**. Presumably, this is the first information concerning the formation of a phosphorus ylide from a trivalent phosphorus compound and an acrylic compound such as acrylonitrile. In later report, Oda and his co-workers[63] have described that triphenylphosphine adds to activated olefins such as acrylonitrile, ethyl acrylate and acrylamide to give the betaines and further that the betaines give rise to the corresponding ylides **75** which can be captured by benzaldehyde in Wittig olefin syntheses. If the phosphorus ylide **75** (Y=CN) was trapped with propionaldehyde, the product was an olefinic cyanide **76** (Y=CN, R=C_2H_5) with the *cis*-isomer predominating, and in the case with benzaldehyde the *trans*-isomer in the product **76** (Y=CN, R=C_6H_5) was found to be predominant.[64] Further, Trippett[65] has shown that when the phosphines such as **77**, **78**, and **79**, where R″ is a group capable of stabilizing an adjacent carbanion, are treated with the activated olefins the intermediate betaines transfer a proton forming the more stable ylides **80** which can be used *in situ* in Wittig olefin syntheses. The betaine **82** formed from diphenyl-1-phenylvinylphosphine (**81**) and acrylonitrile cyclize to a five-membered ylide **83**, which is further reacted with benzaldehyde and with *p*-tolualdehyde to afford **84** and **85** respectively.[66] No product of a Wittig reaction was isolated from a mixture of tricyclohexylphosphine, an acrylic compound such as acrylonitrile or methyl acrylate, and an aldehyde kept under conditions which seem to be suitable for yielding the product of the Wittig reaction. Instead, a secondary alcohol formulated as **88** was isolated.[67] The result of this reaction is consistent with the reaction process which does not involve the conversion of the initially formed betaine **86** to the corresponding ylide **87**. Recently, Fauduet and his co-worker[68] have described a unique method for the preparation of substituted cyclopropanes **90** by condensing acrylonitrile or methyl acrylate with the betaines **89**, derived from hexamethylphosphorous triamide and some 1, 2-dicarbonyl compounds. They have further described that the reaction proceeds by a nucleophilic attack of the initially formed betaine **89** on the electrophilic carbon atom of the acrylonitrile or methyl acrylate followed by a cyclization accompanying the release of hexamethylphosphoric triamide.

$$(C_6H_5)_3P + CH_2{=}CHCN \longrightarrow \underset{(\mathbf{72})}{(C_6H_5)_3\overset{+}{P}CH_2\text{–}\overset{-}{C}HCN} \longrightarrow \underset{(\mathbf{73})}{(C_6H_5)_3\overset{+}{P}\overset{-}{C}HCH_2CN}$$

$$\xrightarrow{CH_2{=}CHCN} (C_6H_5)_3\overset{+}{P}\underset{\displaystyle CH_2\overset{-}{C}HCN}{CHCH_2CN} \longrightarrow NCCH_2\overset{\displaystyle CHCH_2CN}{\overset{\|}{C}H} \longrightarrow$$

$$(NCCH_2CH_2)_2CCH=CHC(CH_2CH_2CN)_2$$
(CN on CCH; CN on CHC)

(74)

$$(C_6H_5)_3P + CH_2=CHY \longrightarrow (C_6H_5)_3\overset{+}{P}CH_2-\overset{-}{C}HY \longrightarrow (C_6H_5)_3\overset{+}{P}\overset{-}{C}HCH_2Y$$

(75)

$$\xrightarrow{RCHO} RCH=CHCH_2Y + (C_6H_5)_3PO$$

(76)

Y=CN, $CO_2C_2H_5$, $CONH_2$

R=C_2H_5, C_6H_5

$$R(R')PCH_2R'' + CH_2=CHY \longrightarrow R(R')\overset{+}{P}CH_2-\overset{-}{C}HY \longrightarrow R(R')\overset{+}{P}CH_2CH_2Y$$
(CH_2R''; $^{-}CHR''$)

(77) R=C_6H_5, R′=$C_6H_5CH_2$, R″=C_6H_5

(78) R=R′=R″=C_6H_5

(79) R=R′=C_6H_5, R″=$CO_2C_2H_5$

(80) $R(R')\overset{+}{P}\overset{-}{C}HCH_2Y$ (CH_2R'')

$$\xrightarrow{R'''CHO} R'''CH=CHR''$$

R‴=C_2H_5, C_6H_5

Y=CN, $CO_2C_2H_5$, $CONH_2$

$$(C_6H_5)_2PC(C_6H_5)=CH_2 + CH_2=CHCN \rightarrow (C_6H_5)_2\overset{+}{P}(C(C_6H_5)=CH_2)(CH_2\overset{-}{C}HCN) \rightarrow (C_6H_5)_2\overset{+}{P}(C^{-}(C_6H_5)-CH_2)(CH_2-CHCN)$$

(81) **(82)** **(83)**

$$\xrightarrow{RCHO} (C_6H_5)_2P(O)CH_2CHCH_2C=CHR$$
(CN; C_6H_5)

(84) R=C_6H_5

(85) R=*p*-$CH_3C_6H_4$

$$(\bigcirc)_3P + CH_2=CHY \longrightarrow (\bigcirc)_3\overset{+}{P}CH_2-\overset{-}{C}HY \xrightarrow{RCHO} (\bigcirc)_3\overset{+}{P}CH_2-CHY$$
($\bar{O}$–CHR)

(86)

$(\bigcirc)_3\overset{+}{P}\overset{-}{C}H-CH_2Y$ **(87)**

$CH_2=CY-CHR$ (OH) ← $(\bigcirc)_3\overset{+}{P}CH_2-\overset{-}{C}Y-CHR$ (OH) **(88)**

Y = CN, CO_2CH_3

R = CH_3, C_2H_5, *n*-C_3H_7, C_6H_5

$$[(CH_3)_2N]_3P + R\text{-}CO\text{-}CO\text{-}R' \longrightarrow [(CH_3)_2N]_3\overset{+}{P}(\text{O, R, R', O}) \xrightarrow{CH_2=CHY} \text{(H, Y, R, COR')}$$

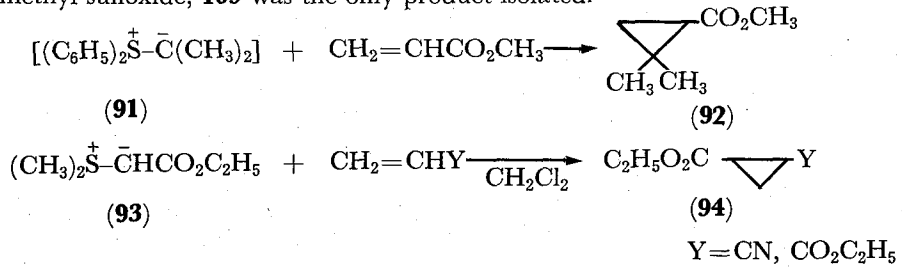
(89) **(90)**

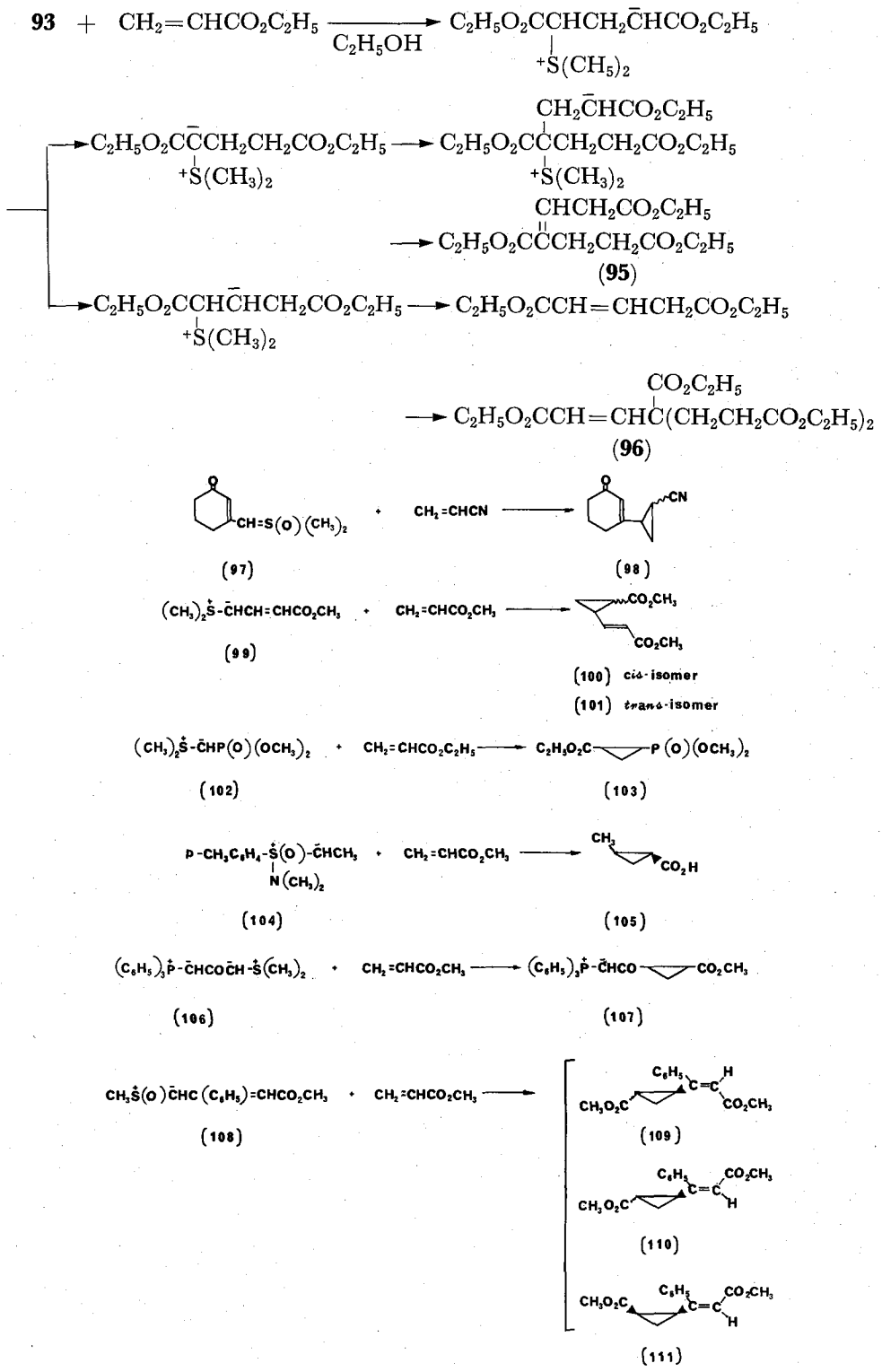
R = C_6H_5, $CO_2C_2H_5$

R′= C_6H_5, OCH_3, OC_2H_5

Y = CN, CO_2CH_3

Sulfonium salts and oxosulfonium salts have alpha C–H bonds which are sufficiently acidic that they may be converted to the corresponding sulfur ylides by treatment with strong bases. There have been several reports concerning the reaction of such the sulfur ylides with acrylic compounds. Corey and his co-worker[69] reported a direct approach to the *gem*-dimethylcyclopropane derivative **92** using the reaction of diphenylsulfonium isopropylide (**91**) with methyl acrylate. The reaction of dimethyloxosulfonium methylide and ethyl acrylate in dimethyl sulfoxide to afford ethyl cyclopropanecarboxylate has also been reported.[70] If substituents that can delocalize negative charge are present at the alpha carbon atom then the sulfur ylides become more stable and can often be isolated. The formation of diethyl 1, 2-cyclopropanedicarboxylate (**94**, Y=$CO_2C_2H_3$) or ethyl 2-cyanocyclopropanecarboxylate (**94**, Y=CN) was achieved[71] by allowing equimolar amounts of ethyl (dimethylsulfuranylidene)-acetate (**93**) and ethyl acrylate or acrylonitrile to react in an aprotic solvent such as dichloromethane at ambient temperature. In both cases the *trans*-isomer predominated. However, the analogous reaction of **93** which was conducted in ethanol solution led not to cyclopropanes but rather to open-chain products of varying complexity.[72] For example, the reaction of **93** with an excess of ethyl acrylate in ethanol at 30–35°C afforded triethyl 2-pentene-1, 3, 5-tricarboxylate (**95**) along with triethyl 3-(2-ethoxycarbonylethyl)-1-pentene-1, 3, 5-tricarboxylate (**96**) with the former predominating. Recently, this kind of reaction has been extended so as to include the case of structurally complex systems containing sulfur ylide moiety. In 1973, Marino and his co-worker[73] described that a carbonyl-stabilized allyloxosulfonium ylide **97** react with acrylonitrile to afford a complex cyclopropane derivative **98**. Dimethylsulfonium 3-methoxycarbonylallylide (**99**), prepared from the corresponding sulfonium bromide and NaH, reacted with methyl acrylate to afford *cis*- (**100**) and *trans*-1-(*trans*-2-methoxycarbonyl) vinyl-2-methoxycarbonylcyclopropane (**101**) with the latter predominating.[74] Also, a sulfur ylide **102** stabilized by a phosphinyl substituent was reacted with ethyl acrylate at room temperature to give a phosphono-substituted cyclopropane **103**.[75] It should be noted that a optically active ylide **104** was generated and reacted with methyl acrylate to afford, after hydrolysis, (+)-(*1S*, 2*S*)-*trans*-2-methylcyclopropanecarboxylic acid (**105**) with an optical purity of 43%.[76] Hercouet and his co-worker[77] have found that a diylide such as **106** also react with methyl acrylate to give a cyclopropane derivative **107** having phosphorus ylide structure. Brule and his co-worker[78] studied the reaction of an oxosulfonium ylide **108** with methyl acrylate in dimethyl sulfoxide, where three products, **109**, **110**, and **111** were isolated. However, when tetrahydrofuran was used as the solvent instead of dimethyl sulfoxide, **109** was the only product isolated.





VI. THE RITTER REACTION AND THE TRANSESTERIFICATION

The well known Ritter reaction has been extended to the addition of acrylonitrile to a variety of compounds capable of forming a carbonium ion such as olefinic compounds, hydroxy compounds and, less commonly, aliphatic aldehydes. These reactions are conducted in concentrated sulfuric acid with or without glacial acetic acid as a diluent, and generally the reaction temperature are mild. Tables I and II summarize data in the literature, but some publications are undoubtedly missed.

Numerous acrylic higher esters can be prepared by heating an appropriate higher alcohol with methyl or ethyl acrylate in the presence of a suitable catalyst, followed by drawing off the produced methyl or ethyl alcohol by azeotropic distillation with the starting acrylate or with reaction solvent, if it was used.

$$\begin{matrix} CH_2{=}CHCO_2CH_3 \\ \text{or} \\ CH_2{=}CHCO_2C_2H_5 \end{matrix} + ROH \xrightarrow{\text{catalyst}} CH_2{=}CHCO_2R + \begin{matrix} CH_3OH \\ \text{or} \\ C_2H_5OH \end{matrix}$$

Table I. The Ritter Reaction of Acrylonitrile with Olefinic Compounds

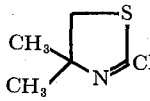
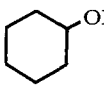
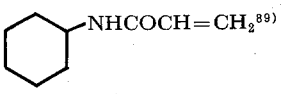
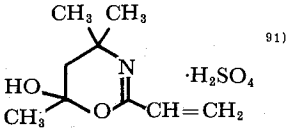
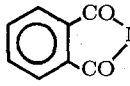
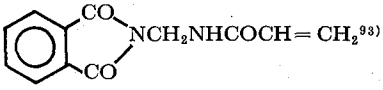
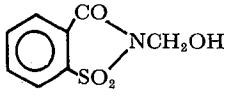
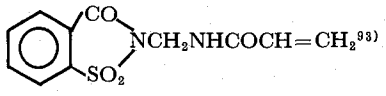
Olefinic compound	Reaction medium	Product
$CH_3(CH_2)_nCH{=}CH_2$	H_2SO_4	$CH_3(CH_2)_nCH(CH_3)NHCOCH{=}CH_2$[79] n=9, 11, 13
$(CH_3)_2C{=}CH_2$	$H_2SO_4+CH_3CO_2H$	$(CH_3)_3CNHCOCH{=}CH_2$[80]
$C_2H_5C(CH_3){=}CH_2$	$H_2SO_4+CH_3CO_2H$	$C_2H_5C(CH_3)_2NHCOCH{=}CH_2$[80]
$CH_2{=}C(CH_3)CH_2Cl$	H_2SO_4	$(CH_3)_2C(CH_2Cl)NHCOCH{=}CH_2$[81]
	H_2SO_4	 $NHCOCH{=}CH_2$[80]
$CH_3COCH{=}C(CH_3)_2$	H_2SO_4	$CH_3COCH_2C(CH_3)_2NHCOCH{=}CH_2$[82]
$(CH_3)_2C{=}CHCO_2H$	H_2SO_4	$HO_2CCH_2C(CH_3)_2NHCOCH{=}CH_2$[83]
$CH_2{=}C(CH_3)CH_2SH$	H_2SO_4	 $CH{=}CH_2$[34]
$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$	H_2SO_4	$CH_3(CH_2)_xCH(CH_2)_yCO_2H$[85] $NHCOCH{=}CH_2$ x+y=15
cis-$CH_3(CH_2)_{13}CH$ $CH_3O_2C(CH_2)_3CH$	H_2SO_4	$CH_3(CH_2)_xCH(CH_2)_yCO_2CH_3$[85] $NHCOCH{=}CH_2$ x+y=17
cis, cis-$CH_3(CH_2)_4CH$ $CHCH_2CH$ $CH(CH_2)_7CO_2C_2H_5$	H_2SO_4	$CH_3(CH_2)_xCH(CH_2)_yCH(CH_2)_zCO_2C_2H_5$[86] $NHCOCH{=}CH_2$ $NHCOCH{=}CH_2$ x+y+z=14

Table II. The Ritter Reaction of Acrylonitrile with Hydroxy Compounds and Aldehydes

Hydroxy compound or aldehyde	Reaction medium	Product
$C_6H_5CH_2OH$	H_2SO_4	$C_6H_5CH_2NHCOCH=CH_2$[87]
$(CH_3)_2CHOH$	H_2SO_4	$(CH_3)_2CHNHCOCH=CH_2$[80]
$(C_6H_5)_2CHOH$	H_2SO_4	$(C_6H_5)_2CHNHCOCH=CH_2$[88]
$(CH_3)_3COH$	$H_2SO_4+CH_3CO_2H$	$(CH_3)_3CNHCOCH=CH_2$[80]
	H_2SO_4	 [89]
$C_6H_5C(CH_3)(OH)CH_2CO_2C_2H_5$	H_2SO_4	$C_6H_5C(CH_3)CH_2CO_2C_2H_5$ (NHCOCH=CH$_2$)[90]
$CH_3COCH_2C(CH_3)_2OH$	H_2SO_4	 [91]
$CH_3COCH_2C(CH_3)_2OH$[a]	H_2SO_4	$CH_3COCH_2C(CH_3)_2NHCOCH=CH_2$[82]
	$H_2SO_4+CH_3CO_2H$	 [93]
	$H_2SO_4+CH_3CO_2H$	 [93]
$(C_6H_5CH_2OH)Cr(CO)_3$	H_2SO_4	$(C_6H_5CH_2NHCOCH=CH_2)Cr(CO)_3$[94]
$C_6H_5COCH_3$	H_2SO_4	$C_6H_5COCH_2C(CH_3)(C_6H_5)NHCOCH=CH_2$[95]
CH_2O	H_2SO_4	$(CH_2=CHCONH)_2CH_2$[96]
CCl_3CHO	H_2SO_4	$(CH_2=CHCONH)_2CHCCl_3$[96]

a) Acetone can be also used instead of diacetone alcohol.[92]

As shown in Tables III and IV, a variety of catalysts have been employed in this transesterification.

VII. SUMMARY

From the foregoing review of the use of acrylic compounds in organic synthesis, it will be seen that the main emphasis has lain in synthetic work, both in the preparation of the useful compounds and in their use as intermediates for further synthesis. There remains, however, large areas of the synthetic chemistry of these compounds, particularly regarding their cycloaddition and dimerization etc., which will latter be described in this bulletin.

Table III. The Reaction of Methyl or Ethyl Acrylate with Some Amino Alcohols

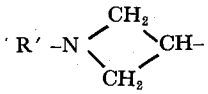
R in ROH and $CH_2=CHCO_2R$	Catalyst used
$R'_2N(CH_2)_nCH(R'')-$ $R'=CH_3$, C_2H_5, n-C_6H_{13} $R''=H$, CH_3 $n=1$, 2	$ZnCl_2$, $Zn(O_2CCH_3)_2$, $Zn(C_2H_5)_2$[97]
$(CH_3)_2N(CH_2)_2-$	CaO, $Ca(OH)_2$[98]
$R'_2NCH_2CH_2-$ $R'=CH_3$, C_2H_5	$(n$-$C_4H_9)_2Sn(O_2CR'')_2$[99] $R''=CH_3$, lauryl
	$(CH_3CO_2)_2Pb\cdot 3H_2O$[100]
$(CH_3)_3CNHCH_2CH_2-$	$Al(O$-iso-$C_3H_7)_3$[101]
$(C_2H_5)_2NCH_2CH_2OCH_2CH_2-$	$Al(O$-iso-$C_3H_7)_3$[102]
 $R'=iso$-C_3H_7, C_6H_5	Na[103]
$(CH_3)_3CNHCH_2CH_2-$ $(CH_3)_3CNHCH_2CH(CH_3)-$ $CH_3CH_2CH_2C(CH_3)_2NHCH_2CH_2-$ $CH_3CH_2CH_2C(CH_3)_2NHCH_2CH(CH_3)-$	CH_3ONa, C_2H_5ONa, $Ti(O$-iso-$C_3H_7)_4$, $Ti(O$-n-$C_4H_9)_4$, $Ti(O$-iso-$C_4H_9)_4$[104,105]

Table IV. The Reaction of Methyl or Ethyl Acrylate with Numerous Hydroxy Compounds other than Amino Alcohols

R in ROH and $CH_2=CHCO_2R$	Catalyst used
$CH_3(CH_2)_3CH(C_2H_5)CH_2-$	$TlOC_2H_5$,[106] C_6H_5ONa[107]
$(CH_3)_2C(OCH_3)CH_2CH(CH_3)-$	p-$CH_3C_6H_4SO_3H$[108]
n-C_4H_9-	p-$CH_3C_6H_4SO_3H$,[109] BaO,[110] Tl_2O_3,[110]
	MoO_3,[110] KU 2/8 cation exchanger[111]
$-CH_2CH_2OCH_2CH_2-$	$Ti(O$-iso-$C_3H_7)_4$[112]
Straight and branched higher alkyl (C_{3-20})	$Ti[O-CH_2CH(C_2H_5)(CH_2)_3CH_3]_4$[113]
Straight and branched higher alkyl ($\geqslant C_8$)	p-$CH_3C_6H_4SO_3H$[114]
Straight and branched higher alkyl	Ca β-diketone-chelated catalyst,[115] Fe acetylacetonate[116]
$[(CH_3)_2CHO]_2P(O)CH_2-$	$Ti(O$-n-$C_4H_9)_4$[117]
	Fatty acid metal salt,[118] Rb carbonate,[119] $ArCO_2Na$[120]

$$R'CO_2CH_2CH_2C_nF_{2n+1} + CH_2=CHCO_2C_2H_5 \xrightarrow{p\text{-}CH_3C_6H_4SO_3H} CH_2=CHCO_2CH_2CH_2C_nF_{2n+1}$$ [121]

$R'=H$, CH_3

$n=1-23$

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